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Appln No. 10/634,640

Amdt date March 3, 2006

Reply to Office action of November 3, 2005

REMARKS/ARGUMENTS

Claims 1-33 are pending in the application. In the November 3, 2005 Office action, the Examiner rejected all claims under 35 U.S.C. § 112, second paragraph, as purportedly lacking clarity in their use of the terms "main group halide" and "mixed metal-main group halide." Applicants respectfully traverse this rejection.

The term "main group halide" refers to a compound comprised of a main group element and a halogen. The "main group elements" "are all elements except the transition and rare earth metals." See *General Chemistry Online: Companion Notes: Matter*, page 4, available at <http://antoine.frostburg.edu/chem/senese/101/matter/index.shtml> (copy enclosed). See also *BBC-h2g2 - The Periodic Table of the Elements*, found at <http://www.bbc.co.uk/dna/h2g2/a593110> (copy enclosed), showing the elements in the periodic table divided into three groups: main group, transition metals, and rare earths (lanthanides and actinides).

A "mixed metal-main group halide" is simply a compound comprised of a metallic element, a main group element, and a halogen. See page 9 of Applicants' specification: "In addition to pure compounds such as FeCl₃, main group halides and mixed metal-main group halides (e.g., ternary compounds), as well as mixtures thereof, can alternatively be used. . . ."

Claims 1, 6-11, 18, and 22-27 stand rejected under 35 U.S.C. § 102(b) as purportedly being anticipated by Coleman.* Applicants have amended claim 1 to include the limitations recited in original claim 2. Applicants have also amended claims 4 and 5 to update their dependencies, and claims 18-33 to change the preamble to "composition of matter." No new matter is introduced by the amendments. In addition, Applicants have amended claim 18 to include a missing parenthetical marker, "(a)". Applicants respectfully traverse the § 102 rejection.

* For the Examiner's convenience, a copy of the entire Coleman article is submitted herewith and cited in a concurrently filed Supplemental Information Disclosure Statement.

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As amended, claim 1 recites:

1. A method of decomposing an organic azide, comprising:
allowing an organic azide to contact a catalyst that comprises a metal halide, main group halide, mixed metal-main group halide, or mixture thereof,
wherein the organic azide has the formula



where R is an organic group selected from the group consisting of alkyl, alkyl amino, nitrogen-containing heterocyclic-substituted alkyl, and alkyl amine substituted with at least one alkyl azide group.

Independent claim 18 as amended recites:

18. A composition of matter comprising:
 - (a) an organic azide having the formula



where R is an organic group selected from the group consisting of alkyl, alkyl amino, nitrogen-containing heterocyclic-substituted alkyl, and alkyl amine substituted with at least one alkyl azide group; and

- (b) a catalyst capable of decomposing the organic azide, said catalyst comprising at least one metal halide, main group halide, mixed metal-main group halide, or mixture thereof.

Neither method claim 1 nor composition claim 18, nor any of the claims dependent therefrom, are anticipated by Coleman. Coleman teaches the decomposition of benzazide, $C_6H_5CON_3$, using Lewis acids such as $FeCl_3$, $GaCl_3$, and $AlCl_3$. Benzazide is *not* an organic azide having the formula $R-N_3$ as recited in applicant's claims 1 and claim 18. The organic group in benzazide is a benzoyl group (C_6H_5CO), *not* alkyl, alkyl amino, nitrogen-containing

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heterocyclic substituted alkyl, or alkyl amine substituted with at least one alkyl azide group. The § 102 rejection should be withdrawn.

Moreoever, Coleman only decomposes the benzazide into phenyl isocyanate -- a relatively large species -- and nitrogen. Essentially, only the azide group is decomposing. In contrast, the present invention is useful as a monopropellant for rocket engines, auxiliary power units, and other gas generation applications, as the decomposition products are, for the most part, low molecular weight, gaseous species. Also, Coleman's reaction took place over tens of minutes, which is far too slow to be of use in rocket engine applications.

Claims 12, 15, 16, 28, 31, and 32 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Coleman. At page 3 of the Office action, the Examiner states that "Coleman differs from the claims in that he does not specifically teach that a combination of catalysts is used. . ." In fact, Coleman differs from applicants' claims in a much more significant way: benzazide ($C_6H_5CON_3$) is *not* an organic azide having the formula $R-N_3$ as recited in Applicants' claims. There is nothing in the reference that would suggest to the skilled person a method of decomposing a high-energy organic azide, i.e., an alkyl azide, alkyl amino azide, nitrogen-containing heterocyclic-substituted alkyl azide, or alkyl amino azide substituted with at least one alkyl azide group as recited in Applicants' claims. Consequently, Coleman neither teaches nor suggests the method of decomposing an organic azide (claims 1-17) or the composition of matter (claims 18-33) invented by Applicants.

Applicants respectfully request reconsideration of the rejections and a notice of allowance.

Respectfully submitted,

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EXHIBITS

- **R. Coleman, et al., *Acid Catalysis in the Decomposition of Benzazide*, J. Amer. Chem. Soc., 76, 4534-4538, (Sept. 20, 1954)**
- ***General Chemistry Online: Companion Notes: Matter*, p.1-5, (<http://antoine.frostbury.edu/chem/senese/101/matter/index.shtml>)**
- ***BBC-h2g2 - The Periodic Table of Elements* (<http://www.bbc.co.uk/dna/h2g2/a593110>)**

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tane was used to develop the chromatogram and elute the *p*-nitroiodobenzene.

The positions of the iodobenzene and nitrated isomers could be observed under ultraviolet light. Iodobenzene (bluish-white fluorescence) was eluted first and was followed by *p*-, *m*- and *o*-iodobenzenes (purple fluorescence) in order. Although these were not developed into separate bands, the head of the band was a deeper purple than the latter portions of the band and was found to be nearly pure *p*-isomer.

Material recovered from the head of the purple band melted at 174.8–175.0° and was decomposed without further purification. The activity of the silver iodide counted (0.4999 g.) was 3650 c./min., after correction for decay, compared to an activity of 29,774 c./min. given by silver iodide from the original iodobenzene. From these data and the percentage of *p*-isomer determined above, it was found that the number of millimoles of iodobenzene nitrated was 4.8 ± 0.1.

A similar analysis was carried out on the products of nitration in acetic anhydride. To 35.0 ml. (70%) of the glacial acetic acid solution of the products were added 3.1919 g. of inactive *p*-nitroiodobenzene and 0.07 g. and 1.4 g., respectively, of inactive *m*- and *o*-nitroiodobenzenes. From the acetic acid solution when chilled was recovered 3 g. of crystalline *p*-nitroiodobenzene. This material, 0.5 g. of inactive *o*-nitroiodobenzene and 5 ml. of inactive iodobenzene were dissolved in benzene and chromatographed on a 45-mm. × 70-cm. column of alumina. The *p*-nitroiodobenzene recovered (m.p. 174.8–175.6°) was converted to silver iodide which had an activity of 1076 c./min. The amount of iodobenzene nitrated in acetic anhydride was, therefore, 1.51 ± 0.01 millimoles. When used to calculate the reactivity toward acetyl nitrate of iodobenzene with respect to benzene this gave the values 0.22 ± 0.01 and 0.13 ± 0.01 for nitration in nitromethane and acetic anhydride, respectively.

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[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Acid Catalysis in the Decomposition of Benzazide¹

BY RALPH A. COLEMAN, MELVIN S. NEWMAN AND A. B. GARRETT

RECEIVED APRIL 27, 1954

The rates of Lewis acid catalyzed decomposition of benzazide into phenyl isocyanate and nitrogen have been determined in benzene and nitrobenzene. When the acids were gallium chloride, aluminum bromide, aluminum chloride and ferric chloride, the kinetics of the nitrogen evolution indicates that an acid–benzazide complex formed rapidly, then decomposed slowly by first-order kinetics. Furthermore, the released catalyst does not complex with phenyl isocyanate but immediately recombines with unreacted azide. The decomposition in the presence of antimony pentachloride, titanium tetrachloride, stannic chloride and tellurium tetrachloride were first order with respect to azide and to halide. The rate measurements suggest that the order of decreasing acid strength is as follows: gallium chloride, aluminum bromide, aluminum chloride, ferric chloride, antimony pentachloride, titanium tetrachloride, stannic chloride, tellurium tetrachloride and antimony tetrachloride. Arsenic trichloride, arsenic tribromide, phosphorus trichloride and phosphorus pentachloride were without effect on the decomposition rate.

The decomposition of benzazide into nitrogen and phenyl isocyanate in non-aqueous solvents was found to be catalyzed by protonic acids and by boron fluoride in dioxane.² This suggested that the relative strengths of Lewis acids might be determined by measuring their catalytic effect on the rate of benzazide decomposition. In order that complicating factors such as the formation of carbon dioxide gas³ and products other than phenyl isocyanate be excluded, this study was confined to non-protonic acids in aprotic solvents. In benzene and nitrobenzene solutions, the rate of decomposition of benzazide is increased to varying degrees by soluble metallic halides and could be followed by measurements of the evolved nitrogen.

Experimental

Reagents.—The benzazide, prepared from recrystallized benzhydrazide and nitrous acid, was recrystallized from petroleum ether to a melting point of 27.1–27.2°. The melting point remained unchanged over a period of four months when stored near 0°.

The following C.P. or reagent quality chemicals were distilled in all-glass apparatus at atmospheric pressure (b.p.'s uncorrected): antimony tribromide, 279–281°; antimony trichloride, 217–218°; arsenic tribromide, 215–216°; stannic chloride, 110.5–111°; titanium tetrachloride, 131.5–132.5°; tellurium dichloride, 321.4°; antimony pentachloride 89° at 30 mm. Anhydrous aluminum chloride was

twice sublimed in a stream of dry nitrogen. Gallium trichloride, b.p. 195–196°, was prepared by chlorinating hot metallic gallium. Ferric chloride was prepared from the elements.⁴ Tellurium tetrachloride, formed by chlorinating tellurium dichloride, was distilled. Aluminum bromide (Westvaco) was redistilled, b.p. 349–351°. Boron tribromide, distilled from a mixture of aluminum bromide and sodium fluoroborate,⁵ was redistilled, b.p. 96–97°. Arsenic trichloride, mercuric bromide, phosphorus trichloride and phosphorus pentachloride (all C.P. grade) were used without further purification.

The benzene was C.P. "thiophene free," distilled over sodium. "Pure" grade nitrobenzene was partially crystallized and centrifuged; the crystals were then melted, the liquid dried over phosphorus pentoxide and distilled, b.p. 82–83° at 8 mm.

Apparatus.—A 125-ml. round-bottom reaction flask with a sealed-on water cooled condenser was immersed in a constant temperature bath. The top of the condenser was connected by Tygon tubing to a Hempel gas buret. Changes in atmospheric pressure and temperature were automatically corrected for by balancing a reference reaction flask containing only solvent against the reacting system through a glycol manometer. By doing this, the volume of gas collected was converted to standard conditions with but one conversion factor. During runs, the flask was subjected to pendulum-type agitation.

Procedure.—Twenty-five ml. of solvent was pipetted into a dried reaction flask, then one to three millimoles of the metallic halide was added. After allowing the solution to reach equilibrium temperature, a small tube containing approximately three millimoles of benzazide was placed in the top of the condenser on a movable iron support. The entire gas system was then closed off and balanced against the reference system; the azide was then allowed to drop into the solvent by moving the iron support with a magnet.

(1) Taken from the Ph.D. thesis of R. A. C., The Ohio State University, 1951.

(2) M. S. Newman and H. L. Gildeborn, THIS JOURNAL, 70, 317 (1948).

(3) See M. S. Newman, S. H. Lee and A. B. Garrett, *ibid.*, 69, 113 (1947), for references.

(4) L. F. Audrieth, *et al.*, "Inorganic Syntheses," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, Vol. III, p. 29.

(5) Reference 4, p. 191.

The nitrogen evolved was collected over mercury in a Hempel gas buret; the volumes were corrected for the vapor pressure of solvent and converted to milliliters of nitrogen at 760 mm. and 0°. At least ten measurements were made during the first half-life of the reaction. The reaction temperatures were 54.9° and 10.5°.

Treatment of Data.—The rate of decomposition of benzazide in organic solvents has been shown to follow first-order kinetics,³ the rate constant, k_1 , being calculated from the data through equation 1

$$\log(V_\infty - V) = \frac{k_1 t}{2.303} + \log V_\infty \quad (1)$$

where V is the volume of nitrogen collected in milliliters at time t in minutes, and V_∞ is the total gas collected (usually very close to the theoretical). The decomposition of benzazide in benzene and nitrobenzene followed first-order kinetics for about 70% of the reaction.

When antimony pentachloride, titanium, stannic and tellurium tetrachlorides were used the rate of nitrogen evolution for each kinetic run followed the first-order rate law, equation 1, but the experimental rate constant, k_1 , varied with concentration of the added metallic halide (Fig. 1). This experimental rate constant was resolved into two rate constants by the relationship

$$k^1 = k_1 + k_c(A) \quad (2)$$

where k_1 is the rate constant in the pure solvent, k_c is a catalytic rate constant characteristic of the metallic halide, and (A) is the concentration of the metallic halide (calculated as monomer).

The value of k_c was obtained by plotting k^1 versus concentration of catalyst (A) , the slope of the line being k_c and the intercept when $(A) = 0$ being k_1 (Fig. 1). Data for a typical run treated by equation 2 are shown in Table I. However, for antimony trichloride and antimony tribromide it was necessary to use equation 3 to get constant value for k^1 presumably because antimony trichloride exists chiefly as non-catalytic dimer in solution. The rate constants for all of these cases are listed in Table II.

$$k^1 = k_1 + k_c(A)^{1/2} \quad (3)$$

TABLE I

DECOMPOSITION OF BENZAZIDE ACCORDING TO EQUATION 2,
RUN 61

0.403 g. of benzazide, 0.526 g. (0.077 M) of stannic chloride, 25.6 ml. of nitrobenzene, temperature 54.9°, $(A) = 0.0774$; $k_1 = 0.00098$

$$k_c = \frac{1}{(A)} \left(\frac{2.3}{t} \log \frac{V}{V_\infty - V} - k_1 \right)$$

Time, min.	Vol. N ₂	k_c	Time, min.	Vol. N ₂	k_c
0	0	...	39	37.3	0.280
4	5.5	0.284	47	41.7	.280
8	10.7	.284	61	47.7	.282
11	14.0	.379	69	50.4	.282
14	17.2	.280	77	52.6	.282
20	23.1	.279	89	55.2	.282
28	28.3	.280	107	57.9	.279
32	32.8	.280	63.6 (V _∞)	...	

The data obtained when gallium chloride, aluminum bromide, aluminum chloride and ferric chloride were present always followed over-all first-order kinetics. When benzazide was in excess the reaction

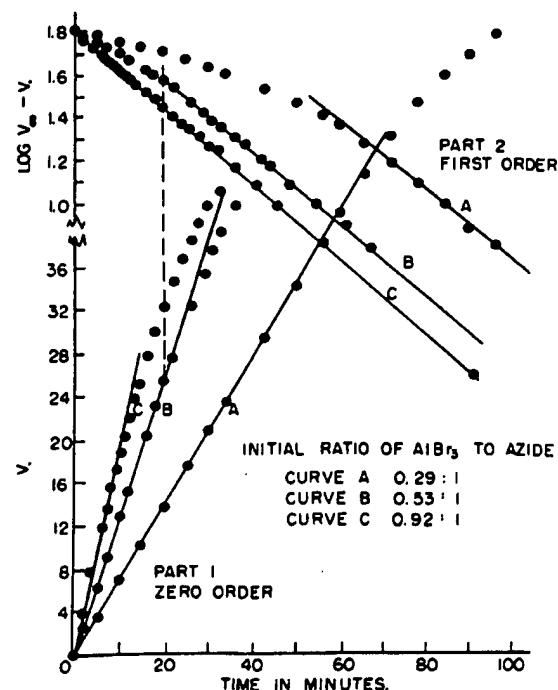


Fig. 1.—Rates of decomposition of benzazide in nitrobenzene in the presence of aluminum bromide at 10.5°. Part I shows zero order when benzazide is in excess at beginning of experiment thus giving constant concentration of active complex; Part 2 shows first-order kinetics of same runs as soon as excess benzazide has decomposed and the concentration of the active complex is changing with time.

TABLE II
CATALYTIC RATE CONSTANT FOR BENZAZIDE DECOMPOSITION

Catalyst	Temp., °C.	Benzene Solvent	Nitrobenzene
None	54.9	6.16×10^{-4}	9.8×10^{-4}
		Class I, rate = $k_c(AZ)^b$	
		k_c	k_1
FeCl ₃	10.5	0.0111
AlCl ₃	10.50340
AlBr ₃	10.5	0.0301	.0376 ^c
GaCl ₃	10.50473
		Class II, rate = $k_1(Z) + k_c(A)(Z)^b$	
		k_1	k_c
TeCl ₄	54.9	0.0232	0.0184
SnCl ₄	54.9	0.0107	.274 ^d
TiCl ₄	54.9	2.34
TiCl ₄	10.50370
SbCl ₄	10.5547
		Class III, rate = $k_1(Z) + k_c(A)^{1/2}(Z)^b$	
SbBr ₃	54.9	0.00088
SbCl ₃	54.9	.00118	0.0113

^a Time in minutes. ^b Where (Z) is concentration of benzazide, (A) is concentration of catalyst (calculated as the monomer), (AZ) is concentration of complex. ^c The same rate constant was obtained in an identical experiment except that one equivalent of phenyl isocyanate was added. ^d In a duplicate experiment an added equivalent of phenyl isocyanate the rate constant was 0.231.

was zero order with respect to benzazide and first order with respect to metallic halide, the data fitting equation 4⁶

$$V = 22,400 k_1(A)t \quad (4)$$

Thus in Fig. 2 a plot of V versus t gives a straight line (zero order in azide) with a slope that varied directly with the amount of catalyst present (first order in catalyst). However, when the reaction had proceeded sufficiently so that benzazide was no longer in excess, the reaction became first order with respect to benzazide and zero order with respect to the catalyst. This is shown in Fig. 2 in

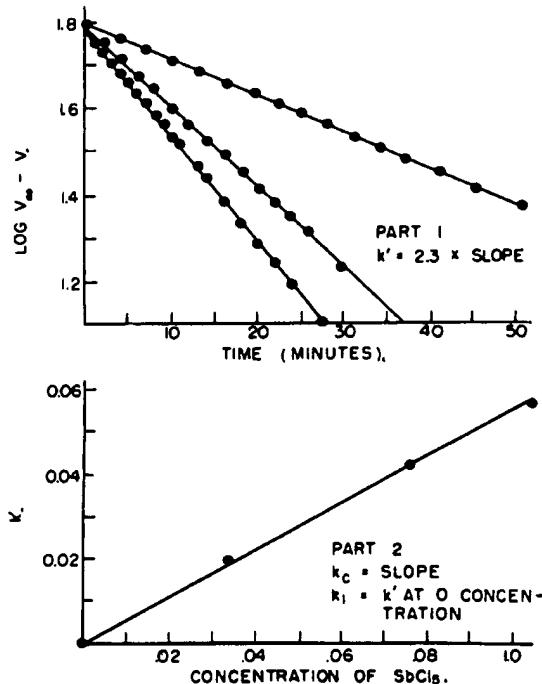


Fig. 2.—The rates of decomposition of benzazide in nitrobenzene in the presence of $SbCl_5$ at 10.5° showing first-order kinetics (Part 1) and method of evaluating k' , k_c and k_1 (Part 1 and 2).

the plot of $\log(V_\infty - V)$ versus time t , which does not become a straight line (first order) until the excess benzazide has been decomposed. The kinetic equation for this case was shown to be

$$\log(V_\infty - V) = -\frac{k_1}{2.3}(t - n) + \log(V_\infty - V_n) \quad (5)$$

where "n" is the time at which the reaction becomes first order in azide and V_n is the volume of nitrogen collected at time n . Data for a typical run treated by equations 4 and 5 are shown in Table III. The rate constants for these several catalysts are listed in Table II.

Arsenic trichloride and tribromide and phosphorus trichloride and pentachloride did not affect the rate of decomposition of benzazide.

(6) Equation 4 is derived from the expression $d(\text{azide})/dt = k_1(A)$ by substituting for (azide) its equivalent, $V_\infty - V/22,400$ (when V_∞ and V have the same significance as before) and for (A) its equivalent (A/v) where A is the number of moles and v is volume of the solution.

TABLE III
DECOMPOSITION OF BENZAZIDE ACCORDING TO EQUATIONS 4 AND 5, RUN 74

0.399 g. of benzazide, 0.257 g. (0.00192 mole) of aluminum chloride and 24.7 ml. of nitrobenzene, temperature 10.5° , $(A) = 0.00192$, $k_1 = V/22,400(A)t$

Time, min.	Vol. N ₂	k_1
0	0	...
3	4.2	0.0326
6	9.0	.0349
8	11.9	.0346
10	14.9	.0346
12	17.9	.0346

$$k_2 = \frac{2.3}{t - n} \log \frac{V_\infty - V_n}{V_\infty - V}$$

(Pseudo zero-order changes to first order)

14(n)	20.7(V _n)	k_2
18	25.9	0.0334
22	30.7	.0346
26	34.8	.0347
31	39.0	.0343
37	43.4	.0345
45	47.9	.0346
50	50.2	.0346
63	54.5	.0346
81	58.0	.0345
92	59.3	.0345
	62.1	...

The following substances are insoluble in nitrobenzene and benzene and therefore could not be studied: lithium chloride, sodium bromide, sodium chloride, cupric chloride, magnesium bromide, mercuric chloride, tellurium dichloride, zinc bromide, bismuth chloride and chromium trichloride.

Boron tribromide was an extremely active catalyst but only 50 to 75% of the expected nitrogen was collected. From the very rapid rate of nitrogen evolution, its rate constant, k_2 , is estimated to be about eighteen times larger than that for gallium chloride.

Discussion

Originally our intention was to classify Lewis acids according to their relative strengths as demonstrated by their ability to catalyze the decomposition of benzazide. However, since more than one kind of kinetics was encountered it is not possible to place all the catalysts in a single strength scale without making some assumptions. Accordingly we have grouped the halides into three classes or series based on the kinetic equation involved. In each case the halides are listed in the order of their relative acid strengths.

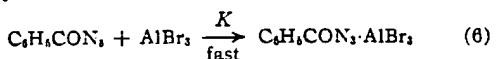
Class I $AlCl_3 > AlBr_3 > AlI_3 > FeCl_3$

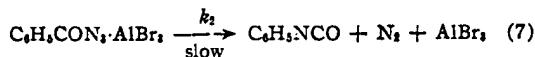
Class II $SbCl_5 > TiCl_4 > TeCl_4$

Class III $SbCl_3 > SbBr_3$

These classes are also listed in the order of decreasing acid strength.

Class I: In this class the rate of formation of the complex with the catalyst is very rapid and the rate-determining step is the decomposition of the complex. This is represented by equations 6 and 7.

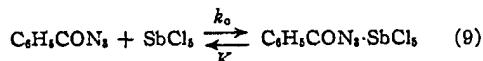




The results of a typical run which fits this scheme are illustrated in Fig. 1. The equilibrium (eq. 6) is attained rapidly and the constant K is large. Hence as long as benzazide is in excess the concentration of the complex remains constant and equal to the concentration of halide introduced at the start of the reaction. The rate for this stage of the reaction is zero order with respect to benzazide and first order with respect to metallic halide. In keeping with this explanation is the fact that the addition of an equivalent of phenyl isocyanate in an experiment at 10° with aluminum bromide in nitrobenzene did not affect the rate constant obtained (0.0376—see Table II). In another experiment in which one millimole of sodium bromide was added to a reaction mixture catalyzed by three millimoles of aluminum bromide in nitrobenzene at 10° , the rate constant was the same as that obtained in a similar experiment involving only two millimoles of aluminum bromide. This result indicates that the millimole of added sodium bromide neutralized one millimole of aluminum bromide according to equation 8.



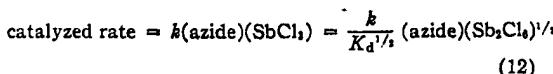
Class II: In this class the rate of formation of the complex may be slow and the rate of decomposition of the complex fast; or the equilibrium between the reactants and the complex may be attained rapidly but the decomposition of the complex may be slow. This is represented by equation 9 and 10.



The results of a typical run which fits this scheme are illustrated in Fig. 2. The kinetics data obtained are consistent with either of the two explanations but are insufficient to decide between the two. If k_c is small and k_2 large, the experimental rate constant would be equal to k_c . On the other hand the equilibrium (eq. 9) may be obtained rapidly and k_2 may be small but K would have to be small to give second-order kinetics. Then the experimental rate constant would be Kk_2 . By either kinetic path the halides comprising this class would appear to be less acidic than those in Class I: either the equilibrium constant is small (implying less coördinating power for the halide); or the rate of formation of the complex is slow (also slower than Class I).

In two comparable experiments in nitrobenzene at 54.9° using stannic chloride, that in which an equimolar amount of phenyl isocyanate was added had a rate constant of 0.231 (compared to 0.274—see Table II). Other experiments, however, showed that the rate constant did not decrease near the end as would be expected if phenyl isocyanate were complexing with catalyst. More work is needed here to clarify the picture.

Class III: In this class, which may be similar to Class I, the question of dimerization of the catalyst must be considered. This involves the additional equation 11



The rates of the reactions in which antimony trichloride is the catalyst can be interpreted readily if the $\text{Sb}_2\text{Cl}_6/(\text{SbCl}_3)_2$ factor is introduced and is assumed to be large; a similar situation obtains with antimony tribromide.

However, it would seem reasonable to expect a similar factor to be required in all cases where dimerization occurs (FeCl_3 , AlCl_3 , AlBr_3 ,⁷ GaCl_3). Van Dyke has shown that aluminum bromide in benzene probably exists as $\text{Al}_2\text{Br}_6\cdot 2\text{C}_6\text{H}_6$. Carlett and Gregory⁸ have shown that two of the halogens (probably of the two bridging halogens) in solid aluminum bromide are only slowly replaced by other halogens.

The idea that antimony trichloride exists in solution as a dimer is not unreasonable as aluminum bromide and chloride have been reported to exist as dimers in solution. That aluminum bromide does not require a square root term in its rate equation can be explained if we assume that it reacts so fast and completely to form the complex, that its rate of dissociation need not appear in the rate-determining step, the decomposition of the complex. On the other hand, it appears that the equilibrium for the dimerization of antimony trichloride is largely in favor of the dimer, so that the concentration of monomer is kept low. This will explain the square root term in equation 12.

However, antimony bromide is reported to be monomeric in benzene.⁹ No data are reported on the chloride.

It is interesting to note that while the rate of the uncatalyzed decomposition of benzazide is greater in nitrobenzene than in benzene, this differential is not maintained for all the catalyzed reactions (see Table II).

TABLE IV
DECREASING ORDER OF ACID STRENGTHS

Acid catalyst	Bond energies	Acid catalyst	Bond energies
GaCl_3	AlI_3	TiCl_4	SnCl_4
AlBr_3	AlBr_3	SnCl_4	ZrCl_4
AlCl_3	AlCl_3	TeCl_4	SbCl_3
FeCl_3	SbCl_3	SbCl_3	
SbCl_3	TiCl_4		

The order of acid strengths of metallic halides found in this work agrees in general with that for their relative effectiveness as catalysts for Friedel-Crafts reactions^{10,11} for the polymerization of isobutene,¹² for the Gattermann-Koch reaction,¹³ and for the dissolution of metals in thionyl chloride.¹⁴ Agreement was found with other methods of meas-

(7) Ross E. Van Dyke, *This Journal*, **72**, 3619 (1950).

(8) John D. Carlett and N. W. Gregory, *ibid.*, **75**, 5238 (1953).

(9) R. Wright, *J. Chem. Soc.*, **109**, 1134 (1916).

(10) O. C. Dermer, D. M. Wilson, F. M. Johnson and V. H. Dermer, *This Journal*, **63**, 2881 (1941).

(11) O. C. Dermer and R. A. Billmeyer, *ibid.*, **64**, 484 (1942).

(12) P. H. Plesch, N. Polanyi and H. A. Skinner, *J. Chem. Soc.*, **257** (1947).

(13) M. H. Dilke and D. D. Bley, *ibid.*, **2613** (1949).

(14) R. A. Hubbard, 2nd, and W. F. Luder, *This Journal*, **73**, 1827 (1951).

uring acid strength such as titration curves,¹⁵ polarization measurements,¹⁶ and bond energy calculations of benzaldehyde-metalllic halide complexes.¹⁷ The bond energies of Dilke and Eley were calcu-

(15) W. S. Peterson, C. J. Heimerzheim and G. B. L. Smith, *This Journal*, **66**, 2403 (1943).

(16) F. Fairbrother, *J. Chem. Soc.*, 503 (1945).

(17) M. H. Dilke and D. D. Eley, *ibid.*, 2601 (1949).

lated from the measured heats of reactions; e.g.,



The comparison of the relative acid strengths from the benzaldehyde decomposition rates (kinetic method) and the bond energy calculations (thermodynamic method), as shown in Table IV is striking.

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TENNESSEE AGRICULTURAL AND INDUSTRIAL STATE UNIVERSITY]

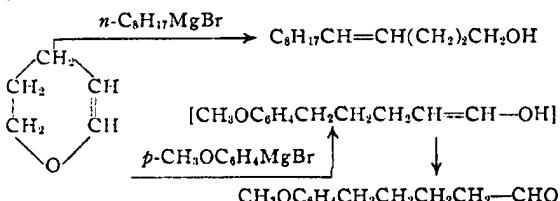
Grignard Reagents and Unsaturated Ethers. III.¹ Reaction of Grignard Reagents with Cyclic Unsaturated Ethers²

BY CARL M. HILL, GILBERT W. SENTER, LONNIE HAYNES AND MARY E. HILL

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The reactivity of cyclic unsaturated ethers with Grignard reagents has been investigated. Results of this study indicate that alkyl and aryl Grignard reagents cleave 2,3-dihydropyran and 4-methyl-3,4-dihydro-2H-pyran at the ether linkage to form unsaturated alcohols and saturated aldehydes. *n*-Hexylmagnesium bromide reacts with 2-nethyl- and 2,5-dimethylfuran to yield β,γ -unsaturated methyl ketones.

Previous papers^{1,3} in this series have illustrated that both aryl and alkyl Grignard reagents cleave aryl substituted vinyl ethyl and allyl alkyl ethers with the formation of aryl and alkyl substituted olefins and alcohols. In the present paper, we have extended these studies to two α,β -unsaturated cyclic ether systems, namely, the furan and dihydropyran. It was postulated that by structural comparison with the open chain vinyl analogs α,β -unsaturated cyclic ethers should be susceptible to reaction with Grignard reagents. The results of the present investigation have fulfilled this prediction. For example, reaction of 2,3-dihydropyran with *n*-octylmagnesium bromide (25% excess) gave as reaction product 4-tridecen-1-ol (36%); while reaction of 2,3-dihydropyran with *p*-anisylmagnesium bromide (25% excess) yielded 5-(*p*-methoxyphenyl)-pentanal (30%).



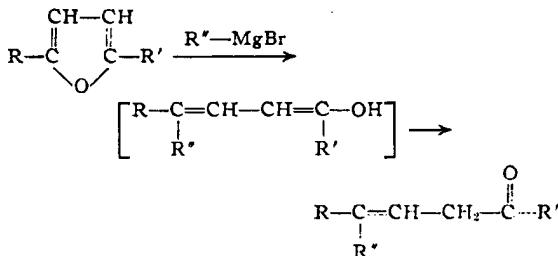
However, when 4-methyl-3,4-dihydro-2H-pyran is allowed to react with *n*-hexyl- and *p*-anisylmagnesium bromides (25% excess), 3-methyl-4-hendecen-1-ol (31%) and 3-methyl-5-(*p*-anisyl)-4-penten-1-ol (40%) are formed, respectively.

Our studies were extended to furans by an investigation of the reaction of 2-methyl- and 2,5-dimethylfuran with *n*-hexylmagnesium bromide which yielded 4-hendecen-2-one (36%) and 5-methyl-4-hendecen-2-one (30%), respectively.

(1) The second paper in this series was published by C. M. Hill, L. Haynes, D. E. Simmons and M. E. Hill, *This Journal*, **73**, 5408 (1953).

(2) This research was supported in part by the United States Air Force under Contract AF 16(600)-466 monitored by the Office of Scientific Research, H. G. Air Research and Development Command.

(3) C. M. Hill, R. A. Walker and M. E. Hill, *This Journal*, **73**, 1663 (1951).



where $R = H$ or CH_3 , $R' = \text{CH}_3$ and $R'' = n\text{-C}_6\text{H}_{13}$. Recent investigations of Fuson and Wallingford⁴ have shown that mesitylmagnesium bromide cleaves 2-mesitylfuran to yield 1-mesityl-4-mesityl-1-hydroxy-1,3-butadiene.

Reaction products were identified through their benzoates or hydrazones and by characterization of their ozonization products. In addition, 4-tridecen-1-ol and 5-methyl-4-hendecen-2-one were converted to the corresponding saturated alcohols.

Acknowledgment.—The authors express thanks to George Canty, who gave valuable assistance in the development of this investigation.

Experimental⁵

Cyclic Unsaturated Ethers.—The 2,3-dihydropyran used in this investigation was purchased from Matheson, Coleman and Bell, Inc., and 2-methyl- and 2,5-dimethylfuran from Eastman Kodak. The 4-methyl-3,4-dihydro-2H-pyran was synthesized according to the procedure reported by Parham and Holmquist.⁶

Reaction of 2,3-Dihydropyran with *n*-Octylmagnesium Bromide.—*n*-Octylmagnesium bromide (1 mole) was prepared under dry nitrogen in the usual manner, and treated with 69 g. (0.8 mole) of freshly distilled 2,3-dihydropyran in an equal volume of absolute ether added during 5 hours. The reaction mixture was refluxed 40 hours and then hydrolyzed with saturated ammonium chloride. The ether layer was separated and the aqueous layer extracted continuously with ether for 36 hours. The ether extracts were combined, dried and concentrated to give a dark residue which was distilled through a Podbielniak column. Fifty-

(4) R. C. Fuson and H. P. Wallingford, *ibid.*, **75**, 5950 (1953).

(5) All melting points are corrected.

(6) W. E. Parham and H. E. Holmquist, *This Journal*, **73**, 913 (1951).

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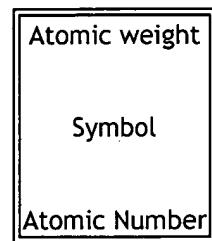
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The Periodic Table of the Elements

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The periodic table of the elements is a nicely organised collection of data about the types of elements (AKA: elements). More detailed information about the table is found in this entry right after this. Just for a quick start: using the table is really quite simple. To save horizontal space this version is subdivided into three parts: The main group elements, the transition metals and the rare earth elements. The group, period and atomic numbers to reconstruct the complete table (it should work like a jigsaw) are as follows:



An asterisk (*) beside the atomic weight indicates that the element is radioactive. The names and symbols are included in a separate table. Further down the entry (after the table part) there is more dedicated to the table itself and to more detailed information about its usage.

The Periodic Table of the Elements

Main Groups

Group	1	2	13	14	15	16	17	18
Period								
1	1.01 H 1							4.00 He 2
2	6.94 Li 3	9.01 Be 4	10.81 B 5	12.01 C 6	14.01 N 7	16.00 O 8	19.00 F 9	20.18 Ne 10

	22.99	24.31	26.98	28.09	30.97	32.07	35.45	39.95
3	Na 11	Mg 12	Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
4	39.10	40.08	69.72	72.61	74.92	78.96	79.90	83.80
5	85.47	87.62	114.8	118.7	121.8	127.6	126.9	131.3
6	Rb 37	Sr 38	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
7	132.9	137.3	204.4	207.2	209.0	209*	210*	222*
	Cs 55	Ba 56	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
	223*	226*						
	Fr 87	Ra 88						

Transition Metals

Group	3	4	5	6	7	8	9	10	11	12
Period										
4	44.96	47.88	50.94	52.00	54.94	55.85	58.93	58.69	63.55	65.39
	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30
5	88.91	91.22	92.91	95.94	97.9*	101.1	103.0	106.4	107.9	112.4
	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48
6	138.9	178.5	180.9	183.8	186.2	190.2	192.2	195.1	197.0	200.6
	†La 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80
7	227*	261*	262*	263*	262*	-	-	-	-	-
	‡Ac 89	Rf 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109	Uun 110	Uuu 111	Uub 112

Rare Earths

†Lanthanoids	138.9	140.1	140.9	144.2	145*	150.4	152.0	157.3	158.9	162.5	164.9	167.3	168
	La 57	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tr 69
‡Actinoids	227*	232.0	231*	238.0	237*	244*	243*	247*	247*	251*	252*	257*	258
	Ac		Pa			Pu	Am	Cm	Bk	Cf	Es	Fm	M

	89	Th 90	91	U 92	Np 93	94	95	96	97	98	99	100	10
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Element name table

Symbol	Name	Symbol	Name	Symbol	Name	Symbol	I
H	Hydrogen	He	Helium	Li	Lithium	Be	E
B	Boron	C	Carbon	N	Nitrogen	O	C
F	Fluorine	Ne	Neon	Na	Sodium	Mg	F
Al	Aluminium	Si	Silicon	P	Phosphorus	S	G
Cl	Chlorine	Ar	Argon	K	Potassium	Ca	C
Sc	Scandium	Ti	Titanium	V	Vanadium	Cr	C
Mn	Manganese	Fe	Iron	Co	Cobalt	Ni	I
Cu	Copper	Zn	Zinc	Ga	Gallium	Ge	C
As	Arsenic	Se	Selenium	Br	Bromine	Kr	E
Rb	Rubidium	Sr	Strontium	Y	Yttrium	Zr	Z
Nb	Niobium	Mo	Molybdenum	Tc	Technetium	Ru	F
Rh	Rhodium	Pd	Palladium	Ag	Silver	Cd	C
In	Indium	Sn	Tin	Sb	Antimony	Te	-
I	Iodine	Xe	Xenon	Cs	Caesium	Ba	E
La	Lanthanum	Ce	Cerium	Pr	Praseodymium	Nd	I
Pm	Promethium	Sm	Samarium	Eu	Europium	Gd	C
Tb	Terbium	Dy	Dysprosium	Ho	Holmium	Er	E
Tm	Thulium	Yb	Ytterbium	Lu	Lutetium	Hf	E
Ta	Tantalum	W	Tungsten	Re	Rhenium	Os	C
Ir	Iridium	Pt	Platinum	Au	Gold	Hg	I
Tl	Thallium	Pb	Lead	Bi	Bismuth	Po	F
At	Astatine	Rn	Radon	Fr	Francium	Ra	F
Ac	Actinium	Th	Thorium	Pa	Protactinium	U	L
Np	Neptunium	Pu	Plutonium	Am	Americium	Cm	C
Bk	Berkelium	Cf	Californium	Es	Einsteinium	Fm	F
Mendelevium	No	Nobelium	Lr	Lawrencium	Rf	F	
Db	Dubnium	Sg	Seaborgium	Bh	Bohrium	Hs	F
Mt	Meitnerium	Uun	Ununilium	Uuu	Unununium	Uub	L

More Detailed Information

The periodic table of the elements is a work of generations of scientists (see: History of the Periodic Table). It is not complete¹ and it is not in its final layout². The artificial elements with the atomic number greater than 94 exist as traces, they are so unstable that only few atoms of these elements have ever been synthesized. The more 'stable' part of the periodic table is widely used in research labs all over the world.

Other Properties of the Elements

Few elements are non-metals. They are: Hydrogen (H), the entire group 18 ('Noble Gases'), Gr, At, Group 16 excluding Po and Te, Group 15 N and P, As is a semi-metal, Group 14 C, Si is a semi-metal, Group 13 only B.

Few elements are gaseous at normal conditions (298 K, 1 atm): H (H_2), N (N_2), O (O_2), F (F_2), Cl, Noble Gases. Only two elements are liquid at normal conditions: Hg and Br.

All elements have a variety of different **isotopes** which are elements with the same nuclear charge but different amount of neutrons. The properties of different isotopes of the same element vary greatly from a chemical point of view. Elements that only have one **natural isotope** are: Be, F, Na, Al, Y, Nb, Rh, I, Cs, Pr, Tb, Ho, Tm, Au and Bi.

The measurement unit of the atomic weight is the amu (atomic mass unit). 1 amu corresponds to the mass of the ^{12}C isotope (it is sort of an average between the mass of protons and neutrons).

How to Use the Periodic Table of Elements

The table is most commonly used to look up the atomic weight of the elements. Those are used to calculate the molar mass of any compound. The molar mass of a compound is the mass in grammes of 6.022 $\times 10^{23}$ molecules of the compound (normally molecules). The number 6.022×10^{23} is also called **one mole** or the **Avogadro number**, more rarely the **Lochschmidt number**⁴.

Example: (To illustrate the usage of moles, atomic weights and the periodic table.) For any reaction, we need one mole of potassium permanganate ($KMnO_4$). She looks at the formula and calculates the number of atoms of each element in one mole of potassium permanganate (by checking the periodic table), one mole of manganese and four moles of oxygen (because there are four oxygens in one unit of the permanganate). She adds the numbers and finds that she needs 209.4 grammes of the potassium permanganate (which is available as a violet, rather than a pink powder). Weighing a powder is more effective and can be done faster than counting all 6.022×10^{23} molecules.

The second most common use of the periodic table is as laboratory-deco. The periodic table is impressed on mouse-pads, t-shirts and posters (in all kinds of design ranging from serious to cartoonish). Something must be wrong if a chemistry office or lab is not decorated with a periodic table so prominently.

Other usages of the periodic table require some experience in chemistry. The periodic table is more complex way than it appears on first sight. The elements are not just ordered according to their atomic number (or weight). The position of an element in the table will tell the scientist something about its properties. This is so, because the elements are also arranged according to their electronic configuration. (Electronic configuration)

How to Use the Periodic Table of the Elements (Advanced)

There are two fundamental trends that go along with the electronic configuration, and the position of an element in the table.

The **electronegativity**⁶ increases from left to right in the periodic table, and decreases with the group number (excluding the noble gases: they do not have an electronegativity).

The **atomic radius** decreases with the group number (from left to right), and increases with the period (from top to bottom).

These properties allow an evaluation of the shape and consistency of the electron shells of a certain element. From this, it is possible to estimate the acidity of the hydrides, the solubility of certain compounds, and the reactivity with other compounds.

Example: What can be predicted for NaBr (sodium bromide) just from the periodic table? Sodium is very electronegative (it is on the very left side of the table), it will lose its electron for any species that want it more dearly (i.e. for anything with a higher electronegativity), like the bromine atom (which is on the right side of the table). The sodium loses one electron and will become positively charged, and the bromine atom will gain a negative charge. Charged elements (also called ions) are known to be well soluble in water. This explanation is descriptive, it helps to get the picture. One must bear in mind, though, that the interactions taking place in a solution are overwhelmingly more complex and exhaustingly difficult to explain.

Other stuff worth knowing

Group-names

As mentioned before, the periodic table is a collection of element-data arranged according to some of their properties. From this arrangement, the groups have received names which are well known. The most well known group-name is probably the *halogens* (or rather unadorned: Group 17). Below follows more detailed information on each group, let there be the remark that hydrogen is a big exception to any group. And here are the group-names:

Alkali metals - Group 1 (excluding hydrogen): The reaction of these elements with water results in a strong base solution, hence the name of the group.

Alkaline-earth metals - Group 2: The reaction with water will also lead to an alkaline solution. The name 'earth' to the denomination of this group is due to the findings of minerals containing these elements.

Triels - Group 13 (or 'boron-group'): This is a synthetic name originating from the time when group 13 was called 'tri' from the greek version of 'three', and 'els' being a new short form for 'element'.

Tetrels - Group 14 (or 'carbon-group'): Same thing happened here. (From *tetra* which is greek for 'four')

Pentels - Group 15 (or 'nitrogen-group'): Same thing with *penta* (greek; meaning 'five')

Chalcogens - Group 16: Elements of this group form ores. (*chalcos* is greek for 'ore' and *genai* means 'to generate' - like in 'genesis')

Halogens - Group 17: Elements of this group form salts. (*halos* the greek word for 'salt' and *genai* means 'snob').

Noble Gases - Group 18 (or 'inert gases'): Elements of this group do not react. And 'noble' sounds like a 'snob'.

Links. The periodic table of the elements in the net.

Webelements.com (very graphic)

IUPAC Homepage (very official)

The Pictorial Periodic Table (very complete)

¹ There is no reason to believe it will ever be complete.

² The systematics of the periodic table have changed quite often. The official numbering of groups and periods and the naming of the new discovered or synthesized elements is done by the International Union of Pure and Applied Chemistry (IUPAC).

³ Amadeo Avogadro (1776-1856), Italian scientist.

⁴ Lothar Meyer was the first to determine the value of Avogadro's number.

⁵ On this level it is of course impossible, and luckily irrelevant, to tell if there are exactly or a few billions or trillions of molecules more or less.

⁶ The electronegativity is a very fuzzily defined measure for the affinity of one atom to take one extra electron into its outer electron-shell (this is something like an orbit around the nucleus). This affinity is due to the fact, that certain shell configurations are very stable (like having all electrons in one shell). Likewise, there is something like an electropositivity, which would be the proneness of one element to lose one electron for the sake of having a complete outer shell (Latter measure is not in use since its definition is even fuzzier). For a more precise explanation see the notes on the IUPAC homepage.

see: electronic configuration

NaBr dissolves well in water, if a silver nitrate (AgNO_3) solution is added, eventually the ions will come close enough and temporarily form the AgBr compound (silver bromide). This compound is not well soluble in water, it will precipitate. Why? The bromine atom is not electronegative enough to completely retain the electron from the silver (it is also on the same side of the table), both atoms will have to share it, they will not form ions which are easily dissolved in water.

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